



EFFECT OF TIN IMPURITY ON THE BAND GAP AND OTHER PARAMETERS OF AMORPHOUS Se-Te THIN FILMS

Vinyas Goswami

Research Scholar

Department of Physics

Sunrise University, Alwar, Rajasthan

Satendra Singh

Associate Professor

Department of Physics

Sunrise University, Alwar, Rajasthan

ABSTRACT:

Thin films of amorphous $\text{Se}_{40-x}\text{Te}_{60}\text{Sn}_x$ glassy alloys have been synthesized by thermal evaporation technique under high vacuum conditions ($\sim 10^{-5}$ torr). The optical spectra of amorphous $\text{Se}_{40-x}\text{Te}_{60}\text{Sn}_x$ ($x = 0, 2, 4, 6, 8$) thin films have been measured by a double beam UV-VIS-NIR computer controlled spectrophotometer over the range of 200-3000 nm. Swanepole technique has been used to calculate the optical constants [refractive index (n), real dielectric constant (ϵ'), imaginary dielectric constant (ϵ'') and absorption coefficient (α)] and optical band gap of amorphous $\text{Se}_{40-x}\text{Te}_{60}\text{Sn}_x$ thin films. Absorption coefficient (α) increases with incident photon energy ($h\nu$) for all the samples. The optical band gap increases with increase of the tin (Sn) content.

Keywords: Chalcogenide glasses, Thin film, Optical constants, Optical band gap etc.

1. Introduction

Amorphous chalcogenide thin films have received a great deal of attention due to a new advanced and replaceable technology material because of their interesting electrical, optical and thermal properties [1-3]. High refractive index ranging and low optical losses permits their development as infrared optical materials [4]. The absence of long-range order in these glasses allows the modification of their optical properties to a specific technological application by continuously changing their composition. The study of optical constant of materials is interesting because of the use of these materials in optical fibers and the optical properties of all materials are related to their atomic structure, electronic and band structure. One of the chalcogenide glass $\text{Se}_{40-x}\text{Te}_{60}\text{Sn}_x$ thin film. Se-Te glassy alloy have gained much importance among chalcogenide glasses because of their high photosensitivity, greater hardness, high crystallization temperature and smaller ageing effect as compare to pure a -Se [5] and useful in practical application [6]. It was believed earlier that impurities have little effect on the properties of amorphous semiconductors as each impurity atom satisfies its requirement by adjusting its neighboring environment. The role of various metals such as Ag, Sn etc. as "additives" in affecting the properties of chalcogenide glasses have been received much attention [7, 8]. It would be interesting to study the role of Ag, Sn metals in affecting the properties of the glasses of the Se-Te system. In this communication, we report the effect of Sn and Ag atom on the optical properties of Se-Te system. Sn is chosen as an additive material because it alloys with most of the metals and modify their

physical properties. The knowledge of accurate values of wavelength dependent refractive index of thin films yields fundamental information on the optical energy gap (E_g), defect levels, phonon and plasma frequencies, etc. The optical behavior of material is utilized to determine its optical constant. Optical constants like refractive index (n) and extinction coefficient (k) are calculated by well known Swanepoel method [9], using transmission spectrum in the UV-VIS-NIR region. Analysis of absorption coefficient was also carried out to determine the E_g and the nature of transitions. The addition of different elements into chalcogenide glasses in order to modify their properties was popular even from the late 60 years. Sn-containing chalcogenide glasses have attracted much interest in glass science and technology for fundamental research of their structure, properties and preparation [10-14]. They have many current applications in optics, optoelectronics, chemistry and biology such as optical elements, gratings, photodoping, optical memories, microlenses, waveguides, holography, bio and chemical sensors, solid electrolytes, batteries etc. [15-24]. The effect of an impurity in an amorphous semiconductor material may be widely different, depending on the conduction mechanism and the structure of material [25]. The impurity may either destroy the dangling bond centres of one sign or form charged centres which are compensated by centers of opposite sign. In the present study work Sn has been

Chosen as an additive element in Se-Te alloys The third element behaves as chemical modifier as it is reported to expand the glass forming region. The addition of third element like Sn in Se-Te binary alloy is expected to change the optical and electrical properties of host alloy. A typical chalcogenide has a relatively sharp optical absorption edge, single electrical activation energy, efficient photo excited conductivity and luminescence. The study of the optical properties of chalcogenide glasses is important for the determination of the electronic band structure as well as other optical parameters, such as optical energy gap and refractive index. The aim of present paper is to study the effect of Sn incorporation on the optical properties of Se-Te alloys. The optical transmission spectra of the amorphous thin films of $a\text{-Se}_{40-x}\text{Te}_{60}\text{Sn}_x$ are measured by spectrophotometer. **2. Experimental Procedure**

Glassy alloys of $a\text{-Se}_{40-x}\text{Te}_{60}\text{Sn}_x$ ($x = 0, 2, 4, 6, 8$) were prepared by melt-quenching technique. The exact proportions of high purity 99.999% Se, Sn and Te granules were weighted according to the formula of $a\text{-Se}_{40-x}\text{Te}_{60}\text{Sn}_x$ ($x = 0, 2, 4, 6, 8$). The powder mixture was loaded into quartz ampoule and sealed under vacuum at 10^{-5} torr. The sealed quartz ampoules was loaded in a furnace and heated to 950°C at a rate of 3-4 C/minute for 18 hours to ensure the composition homogeneity and quenched in liquid nitrogen. The ingots were crushed, separated, grounded and characterized. The glassy nature of alloys was checked with the help of X-ray diffraction technique using Cu-K α radiation. The thin films of chalcogenide were synthesized by thermal evaporation technique under high vacuum conditions ($\sim 10^{-5}$ torr) using a small piece of bulk alloy as a source material and glass as a substrate. The films were kept inside the deposition chamber for 24 hours to achieve the metastable equilibrium. The optical transmission spectra of amorphous $\text{Se}_{40-x}\text{Te}_{60}\text{Sn}_x$ ($x = 0, 2, 4, 6, 8$) thin films have been measured by a double beam UV-VIS-NIR computer controlled spectrophotometer as a function of wavelength.

3. Result and Discussion

The optical system under consideration is amorphous, homogeneous and uniform. By the well

known Swanepole's method, which is based on Mainfacer theory [26], the envelope of the interference maxima and minima occurs in the spectrum and the presence of these maxima and minima position confirmed the optical homogeneity of the deposited film and no scattering and absorption occurs at long wavelengths. This technique has been used by various researchers in chalcogenide glasses [27-28].

3.1 Determination of Optical Constants

By Swanepole's method, the optical parameters are deduced from the fringe patterns in the transmittance spectrum. In the transmittance region where the absorption coefficient ($\alpha = 0$), the refractive index n is given by

$$n = [N + (N^2 - s^2)^{1/2}]^{1/2} \quad (i)$$

where $N = (2s / T_m) - (s^2 + 1) / 2$, s is the refractive index of the substrate and T_m is the envelope function of the transmittance minima.

Where ($\alpha \neq 0$), in the region of weak and medium absorption, the refractive index n is given by

$$n = [N + (N^2 - s^2)^{1/2}]^{1/2} \quad (ii)$$

Where $N = \{2s(T_M - T_m) / T_M T_m + (s^2 + 1) / 2$ and T_m is the envelope function Of the transmittance maxima

In the region of strong absorption, the transmittance decreases drastically and Refractive index (n) can be estimated by extrapolating the values in the other Regions.

If n_1 and n_2 are the refractive indices at two adjacent maxima and minima at λ_1 and λ_2 then the thickness of the film (d) is given by

$$d = \lambda_1 \lambda_2 / 2[\lambda_1 n_2 - \lambda_2 n_1] \quad (iii)$$

The extinction coefficient (k) can be calculated by relation

$$k = \alpha \lambda / (4\pi) \quad (iv)$$

$$= (\lambda / 4\pi d) \ln (1/x)$$

where x is the absorbance and d is the film thickness.

In the region of weak and medium absorption, absorbance (x) can be calculated from the transmission minima T_m and given by the equation

$$x = [E_m - \{E_m - (n^2 - 1)^3 (n^2 - s^4)^{1/2}\} / [(n - 1)^3 (n - s^2)] \quad (v)$$

where $E_m = [(8n^2 s / T_m) - (n^2 - 1)(n^2 - s^2)]$

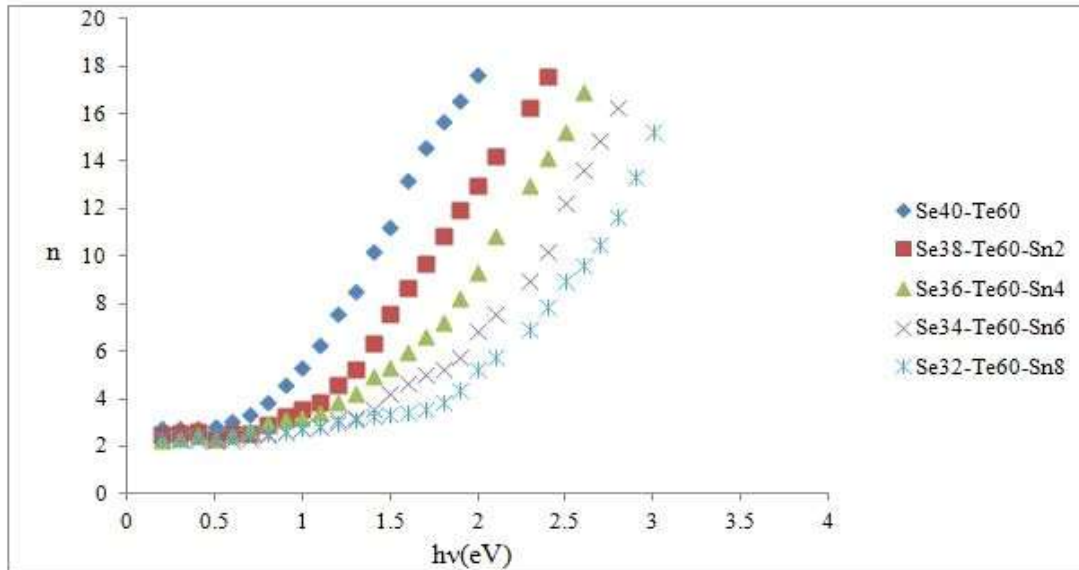


Fig. 1. Variation of refractive index (n) with photon energy (hv) for amorphous $\text{Se}_{40-x}\text{Te}_{60}\text{Sn}_x$ thin films.

The obtained values of refractive index and extinction coefficient are given in Table 1. The variation of refractive index with photon energy (hv) is shown in Fig. 1 and the variation of extinction coefficient with photon energy is shown in Fig. 2. It is observed that the value of refractive index and extinction coefficient show an overall increasing trend with the increase in photonic energy. From Table 1, it is observed that the values of refractive index (n) and extinction coefficient (k) increases with the increase of Sn content for a- $\text{Se}_{40-x}\text{Te}_{60}\text{Sn}_x$ thin films. This spectral and dopant dependence of optical constants with the photonic energy will be helpful in deciding on the suitability of this system for application in optical data storage devices. The real and imaginary parts of the dielectric constant of amorphous thin films has been calculated by the relation respectively

$$\epsilon' = n^2 - k^2 \quad (\text{vi})$$

$$\epsilon'' = 2nk \quad (\text{vii})$$

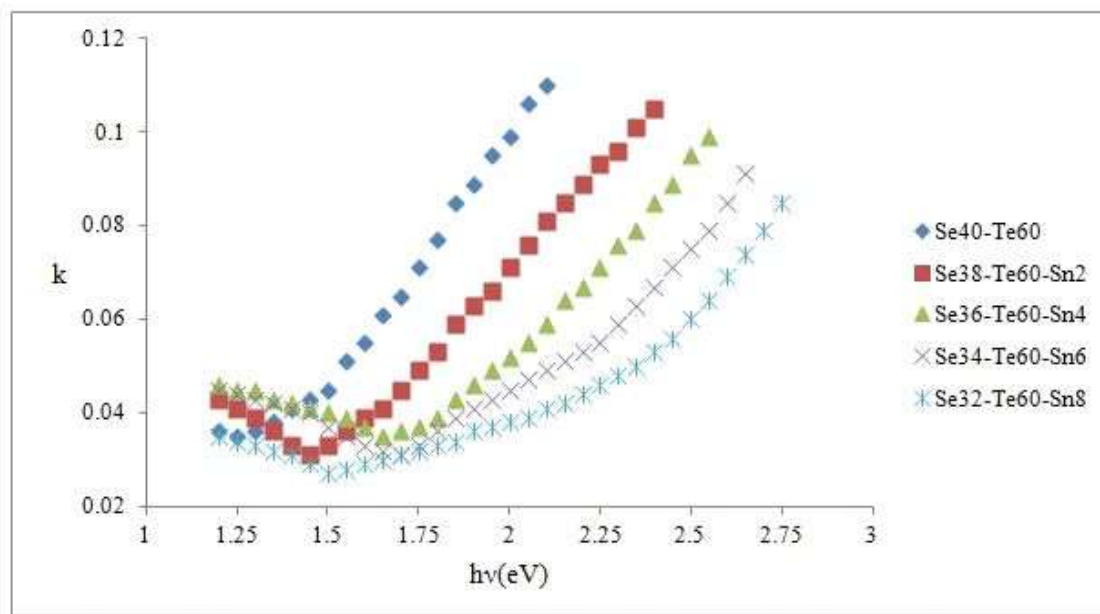


Fig.2. Variation of extinction coefficient (k) with photon energy (hv) for amorphous $Se_{40-x}Te_{60}Sn_x$ thin films.

Material	Refractive Index (n)	Extinction Coefficient (k)	Real Dielectric Constant (ϵ')
$Se_{40}Te_{60}$	17.66	0.099	133.00
$Se_{38}Te_{60}Sn_2$	12.95	0.071	65.00
$Se_{36}Te_{60}Sn_4$	9.35	0.052	50.00
$Se_{34}Te_{60}Sn_6$	6.85	0.045	34.00
$Se_{32}Te_{60}Sn_8$	5.25	0.038	19.00

Table 1: Optical constants for amorphous $Se_{40-x}Te_{60}Sn_x$ thin films at 1600 nm.

	Imaginary Dielectric Constant (ϵ'')	Absorption Coefficient (α) (m^{-1}) $\times 10^3$	Optical Band Gap E_g (eV)
	2.45	28.00	0.78
	1.55	16.00	1.13
	0.79	10.00	1.25
	0.53	6.60	1.33
	0.35	4.10	1.42

The variation of real and imaginary parts of the dielectric constant with photon energy is presented in Figs. 3 and 4 respectively. The calculated values of real part and imaginary part of the dielectric constant are also presented in Table 1. These are found to increase with the increase in photon energy and also with addition of Sn impurity in the present system of $a-Se_{40-x}Te_{60}Sn_x$ thin films.

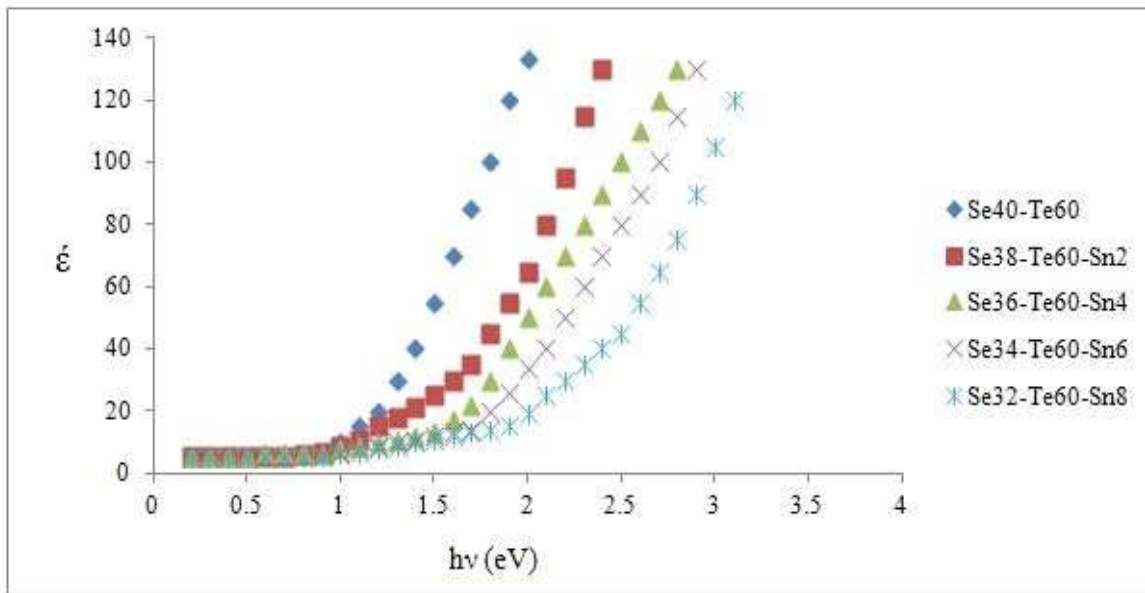


Fig 3. Variation of real dielectric constant (ϵ') with photon energy ($h\nu$) for amorphous $\text{Se}_{40-x}\text{Te}_{60}\text{Sn}_x$ thin films.

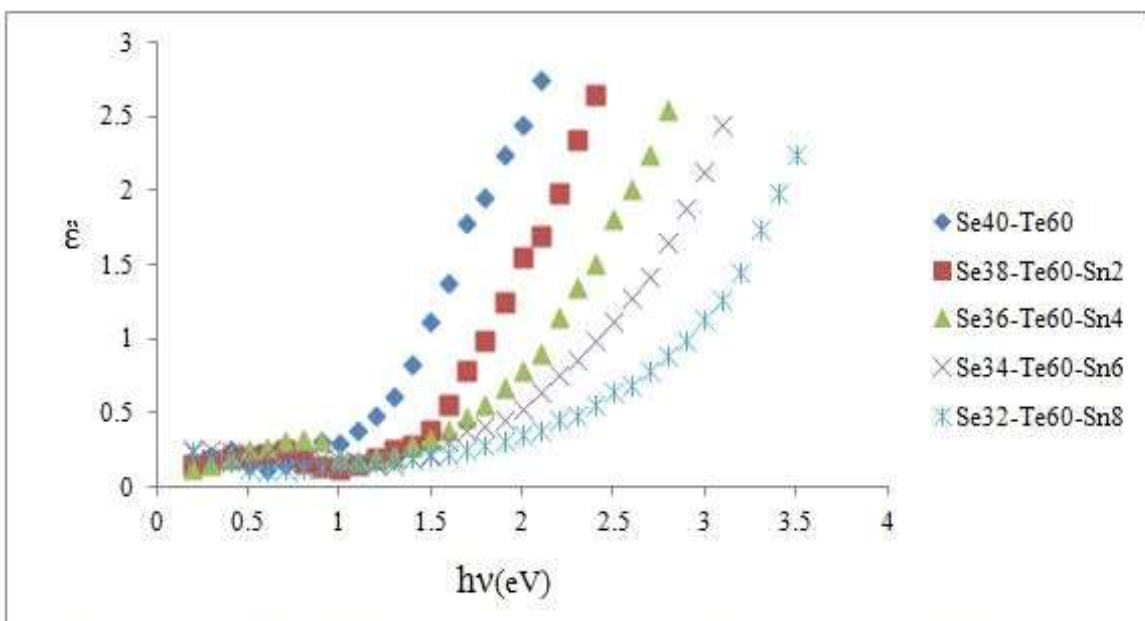


Fig .4. Variation of imaginary dielectric constant with photon energy ($h\nu$) for amorphous $\text{Se}_{40-x}\text{Te}_{60}\text{Sn}_x$ thin films.

3.2 Absorption Coefficient and Optical Band Gap

The absorption coefficient (α) of amorphous $\text{Se}_{40-x}\text{Te}_{60}\text{Sn}_x$ thin films have been Calculated by using relation (viii)

$$\alpha = 4\pi k / \lambda \quad (\text{viii})$$

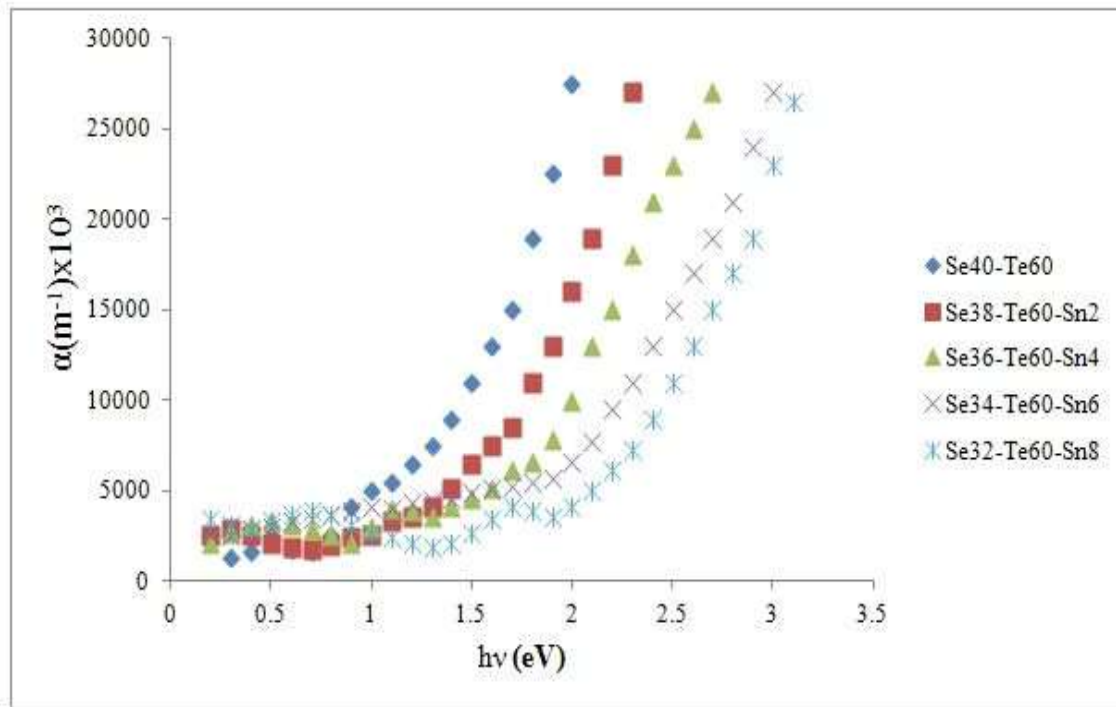


Fig.5. Variation of absorption coefficient (α) with photon energy ($h\nu$) for amorphous $\text{Se}_{40-x}\text{Te}_{60}\text{Sn}_x$ thin films.

Here an increase in the value of absorption coefficient (α) with the increase in photon energy for $\text{a-Se}_{40-x}\text{Te}_{60}\text{Sn}_x$ thin films and it is also observed that the value of absorption coefficient increases with the increase of Sn content. Due to the large absorption coefficient these materials may be suitable for optical memory storage devices. The optical band gap is calculated from absorption coefficient data as a function of energy ($h\nu$) by using Tauc relation [30]. $\alpha = A(h\nu - E_g)^n / h\nu$ (ix) Here A is a constant, E_g is the optical band gap of the material and the exponent n depends on the type of transition and have values $1/2$, 2 , $3/2$ and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively.

The present system of $\text{a-Se}_{40-x}\text{Te}_{60}\text{Sn}_x$ obeys the rule of allowed indirect transition. The values of optical band gap (E_g) is calculated by extrapolating the straight line portion of $(\alpha h\nu)^{1/n}$ vs. $h\nu$ by taking $n = 2$ as shown in Fig. 6. The calculated values of E_g for all samples are given in Table 1. It is evident from Table 1, that the optical band gap (E_g) increases with increase of the Sn content. The increase in optical band gap with increase of the Sn content can be explained on the basis of Mott and Davis Model [29]. According to this technique, chalcogenide thin films contain a high concentration of defect states and these defects are responsible for the presence of localized states in the band gap. The increase in optical band gap with increase of the Sn content may be due to decrease in the density of defect states in the mobility gap or increase in disorderness. The increase in optical band gap along with the decrease in the density of defect states may also be correlated with electro negativity of the elements involved. The electronegativity of Se, Te and Sn are 2.4, 2.1 and 1.96 respectively and Sn has higher electronegativity than Se. The valance band of chalcogenide glasses contains the lone pair p-orbital and addition of electropositive element

(Sn) to electronegative element (Se) may raise the energy of loan pair states, which is further responsible for the broadening of the valance band inside the forbidden gap and leads to band tailing and hence band gap expanding.

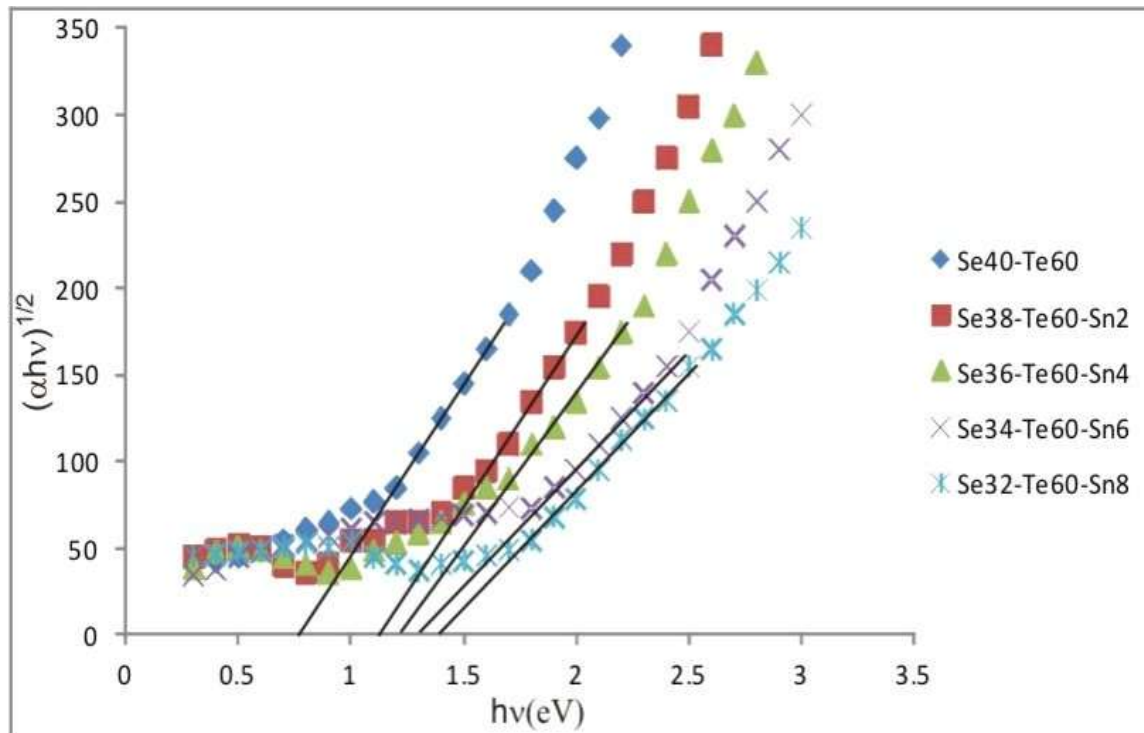


Fig. 6 Variation of $(\alpha hv)^{1/2}$ with photon energy (hv) for amorphous $Se_{40-x}Te_{60}Sn_x$ Thin film

These indirect band gap materials may have potential applications in optical recording media, infrared spectroscopy, laser fibers, xerography, fiber optical telecommunication and electrographic applications. Moreover, their refractive index and transparency in the infrared region are good indicators for integrated optics and detection in the near-infrared spectral domain.

4. Conclusion

The optical gap increases with an increase of Sn concentration in $Se_{40-x}Te_{60}Sn_x$ (where $x = 0, 2, 4, 6$ and 8) systems. The results prove that optical gap strongly depends upon the film composition. The absorption coefficient for the film exhibits a linear dependency on photon energy. In the wide range of wavelength the absorption coefficient follows Urbach relation [31]. It is also found that the values of the optical constants increase with increasing Sn content at room temperature. An increase in the optical band gap with increasing Sn content is probably due to the increase in grain size, reduction in the disorder and decrease in the density of defect state which results in the reduction of tailing of bands.

References

- [1] H.B. Chung, K. Shin, Jae-Min Lee, J. Vac. Sci. Technol. A25, (2006) 48.
- [2] M. S. Kamboj, G. Kaur, R. Thangaraj, D. K. Avasthi, J. Phys. D: Appl. Phys. 35, (2002) 477.
- [3] I.Uddin, H. Howari, and G.A. Ansari Chalcogenide letters Vol.13 (March

2016)pp.117-125

- [4] E.R.Shaaban, M.A. Kaid, E.L. Sayed Moustfa, A. Adel, J. Phy. D: Appl. Phy. 41, (2008) 125307.
- [5] S. O. Kasap, T. Wagner, V. Aiyah, O. Krylouk, Berkirov, L. Tichy J. Mater.Sci. 34, (1999) 3779.
- [6] J. S. Sanghera, L. B. Shaw, I. D. Aggarwal, Comptes Rendus Chimie 5, (2002) 873 .
- [7] N. Mehta, D. Sharma, A.Kumar, Physica B 391, (2007) 108.
- [8] R.S. Kundu, K.L. Bhatia, Nawal Kishore, V.K. Jain, Physica B 74, (1996) 317.
- [9] R. Swanepoel, J.Phys.E: Sci.Instrum. 16, (1983) 1214.
- [10] D. P. Gosain, T. Shimizu, M. Ohmuru, M. Suzuki, T. Bando, S. Okano, J. Mat. Sci. 26,(1991) 3271.
- [11] K. Uchino, K. Takada, T. Ohno, H. Yoshida, Y. Kobayashi, Jpn. J. Appl. Phys. 31, (1993)5354.
- [12] N. Nobukuni, M. Takashima, T. Ohno, M. Ohrie, J. Appl. Phys. 78, (1995) 6980.
- [13] M. Nakamura, Y. Wang, O. Matsuda, K. Inoue, K. Murase, J. Non-cryst. Solids 740, (1996)198-200.
- [14] L. Men, F. Jiang, F. Gan, Mater Sci. Eng. B 18, (1997) 47.
- [15] R. V. Woudenberg, Jpn. J. Appl. Phys. 37,(1998) 2159.
- [16] T. Z. Babeva, D. Dimitrov, S. Kitova, I. Konstantinov, Vacuum 58,(2000) 96.
- [17] I. V. Mikla, I. P. Mikhalko, V. V. Mikla, Mater Sci. Eng. B 83,(2001) 74.
- [18] A. K. Kolobov, J. Tominaga, J. Optoelectron. Adv. Mater 4 (3), (2002) 679.
- [19] S. A. Khan, M. Zulfequar, M. Hussain, Vacuum 72, (2003) 291.
- [20] K. Tanaka, J. Non-cryst. Solids 1179, (1993)164.
- [21] T. Kawaguchi, S. Maruno, S.R. Elliot, J. Appl. Phys. 79, (1996) 9096 .

- [22] M. Ohto, Phys Status Solidi A 159, (1997) 461.
- [23] A. Kumar, P. B. Barman, R. Sharma, Adv. Appl. Sci. Research 1(2), (2010) 47.
- [24] A. Kumar, M. Lal, K. Sharma, S. K. Tripathi, N. Goyal, Chalc. Lett. 9, (2012) 275.
- [25] Arpit Kaistha, V.S. Rangra and Pankaj Sharma, Chalc. Glass Vol. 41, No. 2, (2015) 175-179
- [26] J. C. Manifacier, J. Gasiot, J. P. Fillard, J. Phys. E. Sci. Instrum. 9, (1976) 1002.
- [27] S. M. Ei-Sayed, Vacuum 72, (2004) 169.
- [28] H. S. Metcoally, Vacuum 62, (2001) 345.
- [29] N. F. Mott, E. A. Davis, Electronic Processes in Non-Crystalline Mat., Clarendon, Oxford, (1979) 428.
- [30] M. M. Wakkad, E. Kh. Shoker, S. H. Mohamed, J. Non-Cryst. Solids 157,(2000) 265.
- [31] Urbach Source: Physics Review,13 (1953) 92